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Applicant: Nippon Synthetic Rubber Co. Ltd.
11-24, 2-chome, Tsukiji, Chuo-ku, Tokyo

Inventor: Toshihiko Takahashi
Nippon Synthetic Rubber Co. Ltd., 11-24, 2-chome, Tsukiji, Chuo-ku, Tokyo
Inventor: Takashi Ukachi
Nippon Synthetic Rubber Co. Ltd., 11-24, 2-chome, Tsukiji, Chuo-ku, Tokyo

Assigned representative: Masataka Oshima, patent attorney

Detailed Report

(Name of invention)
adhesive

Abstract
(Object)

This invention offers an adhesive which maintains adequate adhesion even when exposed to visible light or UV without discoloration. When it needs to be removed, it can be removed easily using radiation from a high energy beam such as electron beam, X rays, α -beam, β -beam, or γ -beam.

(Solution)

A adhesive which 100 wt. parts of acryl resin and 1 to 300 wt. parts of a compound which has at least one (meth)acryloyl group in the molecule. It contains practically no photo polymerization initiator, and its adhesion drops when it is irradiated by a high energy beam.

Sphere of the patent application

(Claim 1)

Claim 1 is concerning a adhesive which has the following characteristic: It contains 100 wt. parts of one of the following (co) polymers: (A) (meth)acrylate, ester (meth)acrylate and (meth)acryl amide and 1 to 300 wt. parts of a compound which has at least one (meth)acryloyl group in the molecule. It contains practically no photo polymerization initiator, and its adhesion does not drop when it is irradiated by (B) rays with 300 nm or higher wavelength but adhesion drops when it is irradiated by a high energy beam.

Detailed explanation of the invention

[0001]

(Technical field that this invention belongs to)

This invention is concerning an adhesive. In more detail, it is concerning a high strength adhesive for various kinds of metals, plastics, or glass before irradiating it with a high energy beam such as electron beam, X rays, α -beam, β -beam, or γ -beam. However, after irradiating it using a high energy beam such as the above, its adhesion to these objects drops considerably, and it can be easily removed.

[0002]

(Prior art)

In the past, adhesive used for adhesive tape, etc., had almost the same adhering strength during application as when it is applied to an object. A high-strength adhesive cannot be removed easily when desired. On the contrary, with adhesive which has been designed to be released easily, the necessary adhering strength cannot be acquired.

[0003] In order to solve the above problem, in the past, a component which crosslinks by heat or by photo irradiation is added to the adhesive composition. Then, when it is to be removed, it can be heated or irradiated to generate a three-dimensional crosslinked structure. This reduces adhering strength for easy removal.

[0004] However, when adhering strength is reduced by adding crosslinking components to the adhesive and heating it, the substrate may be deformed, discolored, or deteriorated. In addition, when adhesive which crosslinks even at a relatively low temperature is used to protect the substrate, crosslinking occurs naturally with time at normal temperature, and the adhering strength is reduced gradually.

[0005] Adhering strength is reduced by irradiating an adhesive containing a component which crosslinks by irradiation for an adhesive tape called as dicing tape which is used when IC wafers are cut into individual IC chips in the semiconductor industry (Refer to Japan patent No. H 6-16524, No. H 4-300981, and No. H 6-264033). However, with this method, adhesive strength can drop gradually when the device is exposed to normal levels of UV or visible rays.

[0006]

(Problem that this invention tries to solve)

The object of this invention is to offer new adhesive which can maintain adequate adhering strength even when exposed to visible light or UV irradiation without discoloration. When it is to be removed, it can be easily removed by irradiating it with a high energy beam such as electron beam, X rays, α -beam, β -beam, or γ -beam. Another object and merits of this invention will be clear based on the following explanation.

[0007]

(Steps for solution)

According to this invention, the above object of this invention can be attained by using an adhesive with the following characteristics. It contains 100 wt. parts of (co) polymer that contains at least one of the following: (A) (meth)acrylate, ester (meth)acrylate and (meth)acryl amide and 1 to 300 wt. parts of a compound which has at least one (meth)acryloyl group in the molecule. It contains practically no photo polymerization initiator, and its adhesion does not drop when exposed to B) rays with 300 nm or higher wavelength. Adhesion drops when it is exposed to a high energy beam.

[0008] Examples of monomer (A) in the adhesive of this invention include, as stated above, (meth)acrylate, ester (meth)acrylate or (meth)acryl amide. The (meth)acrylate is acrylic acid or methacrylic acid. Examples of ester (meth)acrylate, in other words, ester acrylate or ester methacrylate include, for example, 2-hydroxy ethyl (meth)acrylate, 2-hydroxy propyl (meth)acrylate, 2-hydroxy butyl (meth)acrylate, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, amyl (meth) acrylate, isoamyl (meth)acrylate, pentyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, octyl (meth)acrylate, isoctyl (meth)acrylate, 2-ethyl hexyl (meth)acrylate, nonyl (meth)acrylate, decyl (meth)acrylate, isodecyl (meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate, lauryl (meth)acrylate, tetrahydrofuran (meth)acrylate, butoxy ethyl (meth)acrylate, ethoxy diethylene glycol (meth)acrylate,

benzyl (meth)acrylate, cyclohexyl (meth)acrylate, phenoxy ethyl (meth)acrylate, methoxy ethylene glycol (meth)acrylate, ethoxy ethyl (meth)acrylate, dicyclo pentanyl (meth)acrylate, dicyclo pentenyl (meth)acrylate, tricyclo decanyl (meth)acrylate, isobornyl (meth)acrylate, bornyl (meth)acrylate, and ester (meth)acrylate which has at least one (average) group containing silicone which is indicated by formula (1) in the molecular structure.



[0010] (In the above formula, R¹, R², R³ can be either identical or different, and they indicates alkyl groups with 1 to 6 carbon atoms or alkoxy groups with 1 to 6 carbon atoms. However, at least one of R¹, R², R³ is an alkoxy group with 1 to 6 carbon atoms.)

[0011] The compound above with the group containing silicon may be, for example, (meth)acryloxy methyl trimethoxy silane, (meth)acryloxy methyl triethoxy silane, (meth)acryloxy methyl tripropoxy silane, (meth)acryloxy methyl tributoxy silane, (meth)acryloxy methyl trihexyl oxy silane, 3-(meth) acryloxy propyl methyl dimethoxy silane, 3-(meth) acryloxy propyl trimethoxy silane, 3-(meth) acryloxy propyl methyl diethoxy silane, 3-(meth) acryloxy propyl methyl dibutoxy silane, etc. As (meth)acryl amide, for example, diacetone (meth)acryl amide, isobutoxy methyl (meth)acryl amide, N,N-dimethyl (meth)acryl amide, t-octyl (meth)acryl amide, dimethyl aminoethyl (meth)acryl amide, diethyl aminoethyl (meth)acryl amide, 7-amino-3, 7-dimethyl octyl (meth)acryl amide, N,N'-dimethyl aminopropyl (meth)acryl amide, (meth)acryloyl morpholine are listed. Monomer (A) can be used either alone or by mixing two or more kinds. Monomer (A) usually makes up at least 40 wt. %, preferably 50 wt. % or more of polymer (A).

[0012] A monomer other than monomer A (called "monomer (B)" in the following) which contains a polymerizing double bond that can be copolymerized with monomer (A) can also be a component of copolymer (A). Examples of this monomer (B) include N-vinyl pyrrolidone, N-vinyl caprolactam, vinyl acetate, vinyl propionate, maleic anhydride, itaconic acid, fumaric acid, (meth)acrylate, (meth)acrylo nitrile, styrene, etc. Monomer (B) can be used either alone or by mixing two or more kinds.

[0013] Polymer (A) can be manufactured by radical polymerization methods, anionic polymerization methods, or cationic polymerization methods suitable for monomer (A) and monomer (B).

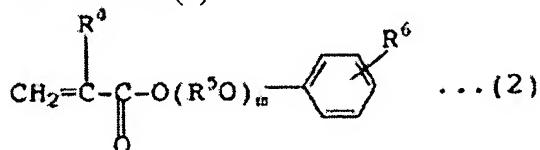
[0014] The polystyrene conversion average molecular weight (called Mw in the following) measured by gel permeation chromatography should be 5 x 10³ to 5 x 10⁶. If the Mw is lower than 5 x 10³, sufficient adhesion strength cannot be acquired. Also, adhesive composition is transferred and deposited on the object of adhesion after irradiation by high energy beam. On the other hand, if the Mw exceeds 5 x 10⁶, mutual solubility with the compound with at least three (meth)acryloyl groups in the molecule may drop.

[0015] Examples of the compound which has at least one (meth)acryloyl group in the molecule used in this invention include 2-hydroxy ethyl (meth)acrylate, 2-hydroxy propyl (meth)acrylate, 2-hydroxy butyl (meth)acrylate, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, butyl (meth)acrylate, amyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, pentyl (meth)acrylate, isoamyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, octyl

(meth)acrylate, isoctyl (meth)acrylate, 2-ethyl hexyl (meth)acrylate, nonyl (meth)acrylate, decyl (meth)acrylate, isodecyl (meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate, lauryl (meth)acrylate, tetrahydro furfuryl (meth)acrylate, buoxy ethyl (meth)acrylate, ethoxy diethylene glycol (meth)acrylate, benzyl (meth)acrylate, cyclohexyl (meth)acrylate, phenoxy ethyl (meth)acrylate, polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, methoxy ethylene glycol (meth)acrylate, ethoxy ethyl (meth)acrylate, methoxy polyethylene glycol (meth)acrylate, methoxy polypropylene glycol (meth)acrylate, dicyclo pentadiene (meth)acrylate, dicyclo pentanyl (meth)acrylate, dicyclo pentenyl (meth)acrylate, tricyclo decanyl (meth)acrylate, isobornyl (meth)acrylate, bornyl (meth)acrylate, diacetone (meth)acryl amide, isobutoxy methyl (meth)acryl amide, N-vinyl pyrrolidone, N-vinyl caprolactam, N,N-dimethyl (meth)acryl amide, t-octyl (meth)acryl amide, dimethyl amino ethyl (meth)acrylate, diethyl amino ethyl (meth)acrylate, 7-amino-3,7-dimethyl octyl (meth)acrylate, N,N-diethyl (meth) acryl amide, N,N'-dimethyl aminopropyl (meth)acryl amide, (meth)acryloyl morpholine, and mono(meth) acryl compound which is expressed by the following formulae (2) to (4);

[0016]

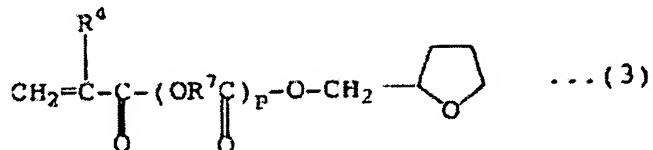
chemical formula (2)



[0017] (In the above formula, R4 is a hydrogen atom or methyl group; R5 is an alkylene group with 2 to 6, preferably 2 to 4 carbon atoms; R6 is hydrogen atom or alkyl group with 1 to 12, preferably 1 to 9 carbon atoms; m is integer from 0 to 12, preferably 1 to 8.)

[0018]

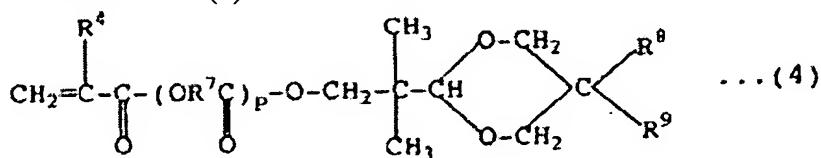
chemical formula (3)



[0019] (In the above formula, R4 is the same as the above; R7 is an alkylene group with 2 to 8, preferably 2 to 5 carbon atoms; p is integer from 0 to 8, preferably 1 to 4.)

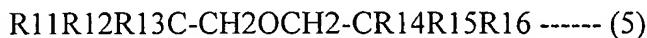
[0020]

chemical formula (4)



[0021] [In the above formula, R4, R7, and p are the same as the above. R8 and R9 are hydrogen atoms, alkyl groups with 1 to 6 carbon atoms, or groups expressed by -R10-A (R10 is an alkylene group with 1 to 6 carbon atoms; A indicates a (meth)acryloyl oxy group).]

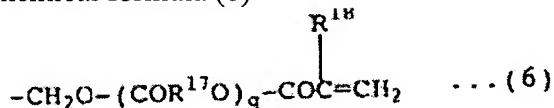
[0022] (continuing from paragraph [0015]) ---- Ethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, 1,4butane diol di(meth)acrylate, 1,6-hexane diol di(meth)acrylate, neopentyl glycol di(meth)acrylate, trimethylol propane trioxy ethyl (meth)acrylate, tris (2-hydroxy ethyl) isocyanurate di(meth)acrylate, tricyclo decane dimethanol di(meth)acrylate, diacrylate such as epoxy (meth)acrylate which has added (meth)acrylate to diglycidyl ether of bisphenol Al; trimethylol propane tri (meth)acrylate, penta erythritol tri(meth)acrylate, trimethylol propane trioxy ethyl (meth)acrylate, tris (2-hydroxy ethyl) isocyanurate tri(meth)acrylate, penta erythritol tetra (meth)acrylate, ditrimethylol propane tetra (meth)acrylate, dipenta erythritol monohydroxy penta (meth)acrylate, dipenta erythritol hexa (meth)acrylate, hexa methylol melamine tri(meth)acrylate, hexamethylol melamine tetra (meth)acrylate, hexamethylol melamine penta (meth)acrylate, hexamethylol melamine hexa (meth)acrylate, compound expressed by the formula (5) below;



[(In the above formula, R11, R12, R13, R14, R15, and R16 are either the same or different, and they indicate any of the organic groups indicated by the following formulae (6), (7), (8), and (9). However, at least three of them - R11, R12, R13, R14, R15, and R16 - have to be organic groups indicated by any of the formulae (6), (7), and (8).

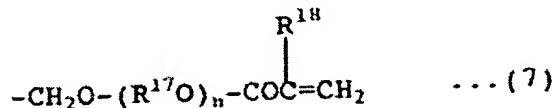
[0023]

chemical formula (6)



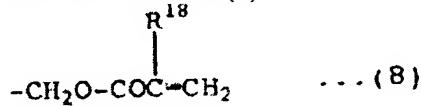
[0024]

chemical formula (7)



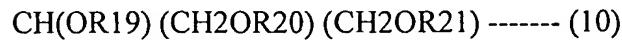
[0025]

chemical formula (8)



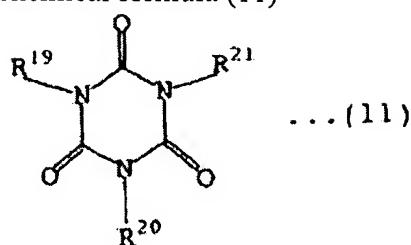
[0026] $-\text{CH}_2\text{OH} \quad \dots (9)$

(In the above formulae, R17 indicates an alkylene group with 2 to 6 carbon atoms; R18 indicates a hydrogen atom or methyl group; q, n each indicate integers from 1 to 5), or a compound which is indicated by the following formula (10) or formula (11);



[0027]

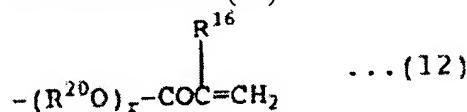
chemical formula (11)



[0028] (In the above formula, R19, R20, R21 can be either the same or different, and they indicate organic groups expressed by the following chemical formula (12)).

[0029]

chemical formula (12)



[0030] (In the above formula, R20 indicates an alkylene group with 2 to 6 carbon atoms; R16 indicates a hydrogen atom or methyl group; r indicates an integer from 1 to 5.)

[0031] (continuing from paragraph [0015]) Above are examples of polyfunctional acrylate.

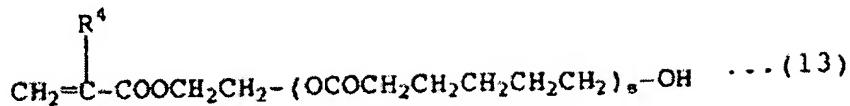
[0032] Products currently on the market include Aronix M111, M113, M114, M117 (manufactured by Toga Synthetic Chemical); KAYARAD TC110S, R629, R644 (manufactured by Nippon Kayaku); Biscoat 3700 (manufactured by Osaka Yuki Kagaku); Yupimar UV, SA1002, SA2007 (manufactured by Mitsubishi Yuka); Biscoat 700 (manufactured by Osaka Yuki Kagaku); KAYARAD R-604, DPCA-20, -30, -60, -120, HX-620, D-310, D-330 (manufactured by Nippon Kayaku); Aronix M-210, M-215, M-315, M-325 (manufactured by Toa Synthetic Chemical), etc.

[0033] It is also possible to use urethane acrylate. Examples include urethane reaction products of (meth)acrylate compounds which contain hydroxyl groups and polyisocyanate compounds, reaction products of (meth)acrylate compounds which contain a hydroxyl group and polyisocyanate compound and alcohol group, reaction products of (meth)acrylate compounds which contain hydroxyl groups and polyisocyanate compound and polymer diol compound, reaction products of (meth)acrylate compounds which contain hydroxyl groups and polyisocyanate compound and alcohol group and polymer diol compounds, etc.

[0034] Examples of (meth)acrylate compounds which contain hydroxyl group include, for example, 2-hydroxy ethyl (meth)acrylate, 2-hydroxy propyl (meth)acrylate, 2-hydroxy butyl (meth)acrylate, 2-hydroxy-3-phenyloxypropyl (meth)acrylate, 1,4-butane diol mono(meth)acrylate, 2-hydroxyalkyl (meth)acryloyl phosphate, 4-hydroxy cyclohexyl (meth)acrylate, 1,6-hexanediol mono(meth)acrylate, neopentyl glycol mono(meth)acrylate, trimethylol propane di(meth)acrylate, trimethylol ethane di(meth)acrylate, penta erythritol tri(meth)acrylate, dipenta erythritol penta(meth)acrylate, (meth)acrylate which is expressed by the following general formula (13) or (14), etc.

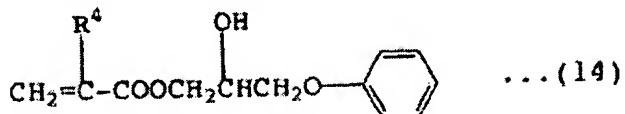
[0035]

chemical formula (13)



[0036]

chemical formula (14)



[0037] (In the above formula, R4 is a hydrogen atom or methyl group; s indicates an integer from 1 to 15.)

Compounds acquired from addition reaction of compounds containing a glycidyl group such as alkyl glycidyl ether, aryl glycidyl ether, glycidyl (meth)acrylate and (meth)acrylic acid can be used as the (meth)acrylate compound which contains a hydroxyl group.

[0038] Examples of the polyisocyanate compound above include, for example, 2,4-thylene diisocyanate, 2,6-thylene diisocyanate, 1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate, 1,5-naphthalene diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, 3,3'-dimethyl-4,4'-diphenyl methane diisocyanate, 4,4'-diphenyl methane diisocyanate, 3,3-dimethyl phenylene diisocyanate, 4,4'-biphenylene diisocyanate, 1,6-hexane diisocyanate, isophorone diisocyanate, 2,2,4-trimethyl hexamethylene diisocyanate, bis (2-isocyanate ethyl)fumarate, 6-isopropyl-1,3-phenyl diisocyanate, 4-diphenyl propane diisocyanate, lysine diisocyanate, water-added diphenyl methane diisocyanate, water-added xylene diisocyanate, tetramethyl xylene diisocyanate, etc.

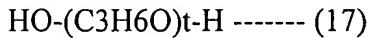
[0039] The alcohol group above may be, for example, methanol, ethanol, n-propyl alcohol, iso-propyl alcohol, n-butyl alcohol, iso-butyl alcohol, sec-butyl alcohol, tert-butyl alcohol, n-amyl alcohol, iso-amyl alcohol, sec-amyl alcohol, tert-amyl alcohol, n-hexanol, cyclohexanol, 4-methyl-2-pentanol, n-heptanol, 3-methyl-1-hexanol, 5-methyl-1-hexanol, 2-ethyl hexyl alcohol, 3,5,5-trimethyl-1-hexanol, n-octyl alcohol, 2-octyl alcohol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, ethylene glycol monohexyl ether, ethylene glycol mono-2-ethylhexyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, diethylene glycol monohexyl ether, diethylene glycol mono-2-ethylhexyl ether, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, triethylene glycol monobutyl ether, tetraethylene glycol monobutyl ether, penta ethylene glycol monobutyl ether, propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, tripropylene glycol monomethyl ether, propylene glycol monoethyl ether, dipropylene glycol monoethyl ether, monohydric alcohol such as benzyl alcohol,

[0040] (poly)ethylene group expressed by general formula (16) such as ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, pentaethylene glycol

$\text{HO-(C}_2\text{H}_4\text{O)}_t\text{-H} \quad \dots (16)$

(In the above formula, t indicates an integer from 1 to 20.)

(poly)propylene glycol group which is expressed by general formula (17) such as propylene glycol, dipropylene glycol, tripropylene glycol, hexapropylene glycol, etc.,



(In the above formula, t indicates an integer from 1 to 20.)

[0041] 1,5-pentadiol, 1,6-hexane diol, glycerin, trimethylol propane and its ethylene oxide-propylene oxide addition bodies, sorbitol, penta erythritol, dipenta erythritol, 1,4-cyclohexane diol, 1,4-cyclohexane dimethanol, 1,2-bis (hydroxyethyl) cyclohexane, 2,2-diethyl-1,3-propanediol, alkylene oxide addition polyol, TMP 30, PNT 4Glycol, EDA, P4, EDA P8 manufactured by Nippon Nyukazai, Cuodole manufactured by Asahi Denka, Tone Polyol 0200, 0221, 0301, 0310, 2201, 2221 manufactured by Union Carbide. These are examples of polyhydric alcohol. The polyhydric alcohol can also be a saturated polyester of these polyhydric alcohols. Examples include reaction products of trimethylol propane and ε-caprolactam, the ethylene glycol group above, propylene glycol group, butylene glycol group, 1,5-pentadiol, 1,6-hexane diol, 1,4-cyclohexane diol, 1,4-cyclohexane dimethanol, 1,2-bis (hydroxyethyl) cyclohexane, 2,2-diethyl-1,3-propanediol, that are reaction products of a 1 mol ratio of saturated dicarboxylic acid per 2 mol of diol. Examples of saturated dicarboxylic acid include oxalic acid, malonic acid, methyl malonate, succinic acid, ethyl malonate, methyl succinate, glutaric acid, adipic acid, 2,2-dimethyl succinate, 2,3-dimethyl succinate, 3-methyl glutarate, 2,2-dimethyl glutarate, 3,3-dimethyl glutarate, pimelic acid, suberic acid, azelaic acid, sebacic acid, etc.

[0042] The amount of compound which has at least one (meth)acryloyl group in the molecule should be 1 to 300 wt. parts, more preferably 5 to 100 wt. parts, per 100 wt. parts of polymer (A). If the amount of compound which has at least one (meth)acryloyl group in the molecule is less than 1 wt. part, crosslinking density by irradiation of high energy beam is low, so the drop in tackiness is small. On the other hand, if the amount of compound which has at least one (meth)acryloyl group in the molecule is more than 300 wt. parts, adhesive tends to transfer when released after irradiating by high energy beam.

[0043] The composition of this invention may include, in addition to polymer (A), a rubber based resin group such as natural rubber, isoprene rubber, styrene butadiene rubber, styrene-butadiene block copolymer, styrene - isoprene block copolymer, butyl rubber, polyisobutylene, silicone rubber, polyvinyl isobutylether, chloroprene rubber, nitrile rubber, graft rubber, reproduced rubber, etc., if necessary.

[0044] When the composition of this invention contains polymer (A) which has a group containing silicon, in order to condense each silicone group in polymer (A), it is possible to add an amine group or organic tin compound to the composition before application. Suitable amine groups include, for example, ethyl amine, diethyl amine, triethyl amine, 1,4-diazabicyclo-2-methyl [2,2,2] octane, γ-(2-aminoethyl)aminopropyl trimethoxy silane, γ-(2-aminoethyl)aminopropyl methyl dimethoxy silane, γ-anilinopropyl trimethoxy silane, γ-dibutyl aminopropyl trimethoxy silane, etc. The organic tin compound may be, for example, di-n-butyl tin dilaurate, bis(2-ethyl hexanate) di-n-butyl tin, tris (2-ethyl hexanate) n-butyl tin, m di-n-butyl tin diehanate, di-n-dicanate di-n-methyl tin, dioctylate,

dilauryl tin, etc. The amount of amine group or organic tin compound is 0.01 to 1 wt. part per 100 wt. parts of total of polymer (A) and compound which has at least one (meth)acryloyl group in the molecule. The composition of this invention contains practically no photo polymerization initiator. If a photo polymerization initiator is used, adhesion drops in a conventional environment which includes irradiation with 300 nm or higher wavelength such as infrared, visible, and UV rays.

[0045] In addition, the composition of this invention may contain tackifiers such as rhodine, hydro rhodine, ester gum, polyterpene resin, polyolefin based resin, polystyrene based resin, aromatic petroleum based resin, alicyclic based hydro petroleum resin, etc. if necessary.

[0046] Furthermore, the composition of this invention may contain anti aging agents, UV absorbing agents, solvent, colorizing agents, photo stabilizers, coupling agents, thermal polymerization prohibitors, leveling agents, surfactants, storage stabilizers, plasticizers, fillers, etc. if necessary.

[0047] Examples of anti aging agents include, for example, Irganox 245, 259, 565, 1010, 1035, 1076, 1081, 1098, 1222, 1330 (manufactured by Chiba Gaigy).

[0048] UV absorbing agents include, for example, Tinuvin P, 213, 234, 320, 326, 327, 328, 329 (manufactured by Chiba Gaigy), SEESORB 102, 103, 501, 202, 712 (manufactured by Cypro Kaseisha). Photo stabilizers include, for example, Tinnuvin 292, 144, 622LD (manufactured by Chiba Gaigy), Sanol LS770, LS 440 (manufactured by Sankyosha), Sumisorb TM-061 (manufactured by Sumitomo Kagakush), etc. Coupling agents include, for example, γ -aminopropyl trimethoxy silane, γ -mercaptopropyl triethoxy silane, γ -methacryloxy propyl triethoxy silane, or as marketed product, SH6020, 6020P, 6062, 6030 (manufactured by Toray - Dow Corning Silicone Co. Ltd.), KB E 903, 603, 403 (manufactured by Shinetsu Kagakusha), etc.

[0049] Solvents include, for example, aromatic hydrogen carbides such as benzene, toluene, xylene, aromatic naphtha; aliphatic hydrogen carbides such as n-hexane, n-heptane, n-octane, n-decane, dipentene, petroleum spirits, petroleum naphtha, turpentine oil; esters such as ethyl acetate, n-amyl acetate, 3-methoxy butyl acetate, methyl benzoate, cellosolve acetate, butyl cellosolve acetate; ketones such as acetone, methyl ethyl ketone, ethyl isobutyl ketone, isophorone, cyclohexanone, methyl cyclohexanone; alcohols such as methyl alcohol, ethyl alcohol, n-propyl alcohol, i-propyl alcohol, sec-butyl alcohol, t-butyl alcohol.

[0050] The composition of this invention can be manufactured by combining the necessary components and optional components appropriately and mixing them by conventional methods.

[0051] The composition of this invention can also be used in the following way. That is, after it is applied on one or both objects to be adhered, it is heated for 1 to 120 minutes at 50 to 150°C, and then the objects are pasted together. In another way, it is applied on one of the objects and after it is heated for 1 to 120 minutes at 50 to 150°C, and an easy-release liner is applied. Next, before use, this easy-release film is peeled off, and the other object to be adhered is pasted together. In another way, it is applied on an easy-release type film, then heated for 1 to 120 minutes at 50 to 150°C, and then applied to the object of adhesion. Next, this easy-release type film is peeled off, and the other object of adhesion is pasted together. In another method, it is applied on an easy-release film, and

it is heated for 1 to 120 minutes at 50 to 150°C. After that, a second easy-release film is applied, and one easy-release film is peeled off. After the other object to be adhered is set in place, the other easy-release film is peeled off, and the other object to be adhered is pasted together.

[0052] Substrates that can be bonded using the composition of this invention include, for example, plastics such as polyethylene, polypropylene, polyvinyl chloride, polyethylene terephthalate, polycarbonate, polysulfone, polymethyl methacrylate, polystyrene, polybutadiene, ABS resin, AS resin, AES resin, nylon, cellulose, nitrocellulose, triacetyl cellulose; thermal curing resins such as phenol formaldehyde resin, cresol formaldehyde resin, melamine resin, urea resin; inorganic substances such as glass, china, porcelain, ceramics, quartz, silicone, iron, copper, aluminum, nickel, etc.

[0053] When these materials are bonded using the composition of this invention, adhesion will be sufficient as long as the bond is not irradiated by a high energy beam such as electron beam, X rays, α -beam, β -beam, or γ -beam. However, when it is irradiated by a high energy beam, adhering strength falls down to 1/10 or less of the value before irradiation, and it can be easily removed.

[0054]

(Examples of practice)

In the following, this invention is going to be explained in more detail using examples of practice. However, this invention is not restricted these examples. In the following, "part" means weight part. Furthermore, Mw of polymer (A) was measured by gel permeation chromatography (GPC) which uses standard polystyrene. Measuring conditions were as follows:

Device: high speed GPC device HLC-802A manufactured by Toso

Detection method: RI

Column: TSK-GEL, G4000 H_{XL}, G3000 H_{XL}, G2000 H_{XL}, (two pieces) manufactured by Toso

Dissolving solvent: tetrahydrofuran, flowing speed: 1.1 ml/min.

Column temperature: 40°C

Tester concentration: 0.006 g/ml (solvent is tetrahydrofuran)

[0055] Polymer concentration after the polymerization reaction was measured after removing the volatile components by heating for 15minutes on a hot plate kept at 230°C. Release strength was measured by performing a T-peel test at 50 mm/min. at 23°C and 50 % relative humidity.

[0056]

Example of practice 1

160 g of methyl methacrylate (1.60 mol), 240 g of n-butyl acrylate (1.69 mol), 100 g of 2-hydroxy ethyl acrylate (0.86 mol), 5 g of 3-(meth)acryloxy propyl trimethoxy silane (0.025 mol), 0.5 g of 2,2'-azobis (isobutyronitrile), and 500 g of methyl ethyl ketone were put in a 2 liter four-opening flask furnished with a stirrer, thermometer, and nitrogen bubbling tube. Stirring and bubbling nitrogen replaced the oxygen in the starting monomer with nitrogen. Next, it was heated by an oil bath to keep the internal temperature at 75 to 85°C. It was stirred for 6 hours and polymerized. The concentration

of the copolymer acquired from the above polymerization reaction was 49.5 %. The average molecular weight of this copolymer was 15,700. The copolymer solution acquired from this reaction is called copolymer solution A in the following.

[0057] After 101 g of copolymer solution A and 25 g of dipenta erythritol hexa acrylate were mixed, it was applied on a PET (polyethylene terephthalate) film (product name: Lumiler, manufactured by Toray) with 75 μm thickness using a 127 μm applicator bar manufactured by Kumagaya Riki Kogyo. It was heated for 20 minutes at 80°C in an air circulation oven, to remove the volatile components, and an adhesive film was manufactured. After this adhesive film was returned to room temperature, a PET film with 25 μm thickness was applied to the adhesive film above. It was left for 1 hour at 23°C and 50 % relative humidity. After that, a portion of the film was cut out, and a release test was administered. It had high release strength such as 1220 g/25 mm. Meanwhile, the remaining film was irradiated by electron beam at an acceleration voltage 165 kV and 1 Mrad from the 25 μm PET film side, but its release strength was very small such as 5 g/25 mm. All of the adhesive was deposited on the 75 μm PET film side, and there was no transfer onto the 25 μm PET film.

[0058]

Example of practice 2

Instead of 25 g of dipenta erythritol hexa acrylate used in example of practice 1, 6 g of trimethylol propane triacrylate was used, and an adhesive was prepared. An adhesive film was prepared the same as example of practice 1, and a release test was administered. It had high release strength such as 930 g/25 mm. Its release strength after irradiating by an electron beam with acceleration voltage 165 kV and 1 Mrad was 10 g/25 mm. This was a considerable drop in release strength. Adhesive transfer did not occur.

[0059]

Example of practice 3

160 g of methyl methacrylate (1.60 mol), 240 g of n-butyl acrylate (1.69 mol), 100 g of 2-hydroxy ethyl acrylate (0.86 mol), 5 g of 3-(meth)acryloxy propyl trimethoxy silane (0.025 mol), 100 g of 2-hydroxy ethyl acrylate (0.86 mol), 0.5 g of 2,2'-azobis (isobutyronitrile), and 500 g of methyl ethyl ketone were put in a 2 liter four-opening flask furnished with a stirrer, thermometer, and nitrogen bubbling tube. While stirring and nitrogen bubbling, the oxygen in the starting monomer was replaced with nitrogen. Next, it was heated in an oil bath to keep the internal temperature at 75 to 85°C. It was stirred for 6 hours, and the polymerization reaction was completed. The concentration of the copolymer acquired from the above polymerization reaction was 49.3 %. The average molecular weight of this copolymer was 16500. The copolymer solution acquired from this reaction is called copolymer solution B in the following.

[0060] 101 g of copolymer solution B and 25 g of dipenta erythritol hexa acrylate were mixed, and an adhesive composition was prepared. An adhesive film was manufactured the same as in example of practice 1, and a release test was administered. It had high release strength such as 1050 g/25 mm. The release strength after irradiation using an electronic with an acceleration voltage of 165 kV and 1 Mrad was as small as 5 g/25 mm, which showed a considerable drop in release strength.

[0061]

Example of practice 4

Instead of 25 g of dipenta erythritol hexa acrylate used in example of practice 3, 15 g of ditrimethylol propane tetra acrylate was used, and an adhesive composition was prepared. An adhesive film was prepared the same as example of practice 1, and a release test was administered. It had high release strength such as 1050 g/25 mm. Its release strength after irradiation using an electron beam with an acceleration voltage of 165 kV and 1 Mrad was as small as 3 g/25 mm, which showed a considerable drop in release strength. Transfer did not occur.

[0062]

Example of practice 5

Instead of 25 g of dipenta erythritol hexa acrylate used in example of practice 1, 15 g of tripropylene glycol diacrylate was used, and an adhesive composition was prepared. An adhesive film was prepared the same as example of practice 1, and a release test was administered. It had high release strength such as 1160 g/25 mm. Its release strength after irradiation using an electron beam with an acceleration voltage of 165 kV and 1 Mrad was as small as 4 g/25 mm, which showed a considerable drop in release strength. Transfer did not occur.

[0063]

Example of practice 6

Instead of 25 g of dipenta erythritol hexa acrylate used in example of practice 1, 15 g of phenoxy ethyl acrylate was used, and an adhesive composition was prepared. An adhesive film was prepared the same as in example of practice 1, and a release test was administered. It had a high release strength such as 1050 g/25 mm. Its release strength after irradiation using an electron beam with acceleration voltage of 165 kV and 1 Mrad was as small as 3 g/25 mm, which showed a considerable drop in release strength. Transfer did not occur.

[0064]

Example of comparison 1

Except that copolymer solution A was used alone as the adhesive composition, an adhesive film was prepared the same as example of practice 1, and a release test was administered. It had small release strength such as 5 g/25 mm. Its release strength after irradiation using an electron beam with acceleration voltage of 165 kV and 1 Mrad was as small as 5 g/25 mm.

[0065]

Example of comparison 2

Copolymer solution B was applied on a PET film and an adhesive film was prepared the same as example of practice 1, and a release test was administered. It had a small release strength such as 5 g/25 mm. Its release strength after irradiation using an

electron beam with an acceleration voltage of 165 kV and 1 Mrad was as small as 5 g/25 mm.

[0066]

(Effects of this invention)

The high energy beam releasing adhesive of this invention can maintain adequate adhering strength even in environments receiving visible or UV irradiation without discoloration. When it is to be removed, it can be easily removed by irradiating it using a high energy beam such as electron beam, X rays, α -beam, β -beam, or γ -beam.